A STUDY OF THE PHOTODEGRADATION OF SELECTED

THERMAL-CONTROL SURFACES

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ABSTRACT

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The results of the Langley participation in the OSO II Round Robin on "Ultraviolet Stability of Thermal-Control Coatings" are presented as well as some recent studies of the ultraviolet stability of a chemical conversion coating (Alodine 401). A preliminary study of the effects of gamma radiation from Cobalt-60 on solar absorptance α_S of several selected white paint-type coatings has shown that the high-energy radiation (electrons and protons) in space can be expected to increase α_S but at a slower rate than the ultraviolet radiation from the sun.

AUTHOR

INTRODUCTION

The highly specialized and diverse nature of space vehicles has greatly influenced the development and testing of thermal-control coatings. In general, these coatings have been developed and tested on a relatively limited basis using custom formulated coatings and individually developed environmental simulation systems. In an attempt to interrelate the environmental testing of various laboratories representing several government agencies, industry, and research institutes, a round robin on the ultraviolet stability of thermal-control coatings was established. This round robin, administered by Carr Neel of NASA Ames Research Center, included laboratory testing of several coatings identical to those to be flown on the Orbiting Solar Observatory II (S-17) experiment during the fall of 1963. The details of the flight results from a related thermal-control experiment (OSO I) have been reported by Neel (refs. 1 and 2). The results of NASA Langley participation in this round robin on "Ultraviolet Stability of Thermal-Control Coatings" are discussed in this report as well as some recent results on the ultraviolet stability of an amorphous aluminum and chrominum phosphate chemical conversion coating (Alodine 401), which was associated with the Echo (A-12) program.

In addition to ultraviolet radiation, the high-energy ionizing radiation in space may also alter the optical properties of thermal-control surfaces.

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However, the literature is meager on this latter aspect of environmental testing of thermal-control coatings. Most studies on the effect of high-energy radiation on optical properties of spacecraft materials have been limited to solar cells and solar-cell covers. A brief study of the effects of high-energy ionizing radiation on several paint-type coatings was carried out to explore the seriousness of this factor. Several organic and inorganic white paints associated with the NASA Ames thermal control experiment on OSO I and OSO II were sealed under vacuum in Pyrex tubes and exposed to the gamma rays from a Cobalt-60 source. The flux of gamma rays in space is quite low; however, the damage from gamma rays are similar to the damage from electrons and protons and offer a convenient means of simulating the effects rather than the environment of the electrons and protons in space.

ULTRAVIOLET STABILITY

Thermal-Control Coatings

The coatings used in the ultraviolet degradation study and their sources are listed in table I.

TABLE I

Coating		Source
Pigment	Vehicle	
Titanium dioxide	Epoxy[a] resin	Lockheed Missiles & Space Co.
Antimony oxide	Potassium silicate	Hughes Aircraft Co.
Zinc oxide	Potassium silicate	IIT Research Institute (formally Armour Research Foundation)
Titanium dioxide	Silicone resin	IIT Research Institute (formally Armour Research Foundation)
Chromium and aluminum phosphates[b]		G.T. Schjeldahl Co.

[a]Skyspar (A-423).
[b]Alodine 401-45.

The first two coatings, based on titanium dioxide-epoxy and antimony oxide-potassium silicate, are known to degrade under ultraviolet radiation as a result of an unstable vehicle and pigment, respectively. The third and fourth coatings, zinc oxide-potassium silicate and titanium dioxide-silicone, represent stable white coatings. These four paint-type coatings were supplied on aluminum test

disks from the Ultraviolet Stability Round Robin. The fifth coating represents a chemical conversion type of surface in which the aluminum substrate contributes significantly to the solar absorptance of the system. These Alodine coatings were received as the outer surface of the 0.75-mil Echo (A-12) laminate and were mounted on test disks by means of G.T. 301 polyester adhesive.

EXPERIMENTAL

Determination of Solar Absorptance

Changes in the optical properties of thermal-control surfaces are a prime criteria for determining their stability to the space environment. The solar absorptance α_s is the optical property of most concern in studying the ultraviolet stability of thermal-control surfaces, since it is this property which is usually most sensitive to ultraviolet effects. The solar absorptance values reported in this paper were determined from measurements of spectral reflectances of the test surfaces over the wavelength range, 0.2 to 2.1 microns. A Cary 14 Spectrophotometer equipped with a barium sulfate-coated integrating sphere attachment (ref. 3) was used for these measurements. Solar absorptance was calculated by summing the average reflectances (between 0.2 and 2.1 microns) in the wavelength increments corresponding to 1 percent of the total of the solar energy using the spectral distribution reported by Johnson (ref. 4). This weighted reflectance was then subtracted from unity to yield the solar absorptance α_s.

Ultraviolet-Vacuum Environmental System

The ultraviolet-vacuum environmental system used in these tests is shown schematically in figure 1. The stainless-steel front plate is integral with the glycol-water-cooled specimen holder which can accommodate up to eight specimens for simultaneous irradiation. The coolant was maintained at $0°$ C with a refrigerated recirculating bath. The temperatures of the test specimens were monitored periodically throughout the tests with copper-constantan thermocouples mounted in the metal substrates of each coating.* Some temperature variations between different samples in the same test were noted and are probably due to differences in sample properties and thermal contact of the test disks with the cooling plate. The vacuum chamber was mounted to a 1,200 liter/sec Ultek ion pump. The vacuum system was allowed to reach an equilibrium pressure of 1×10^{-6} torr before ultraviolet irradiation was initiated. Chamber pressure was monitored throughout the test and maintained in the range of 1×10^{-6} to 6×10^{-7} torr.

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*The substrates for the titanium dioxide-epoxy coating were too thin to permit thermocouple mounting. Sample temperatures were assumed to be comparable to the average of the monitored samples.

High-pressure mercury arc lamps (G.E. BH-6) were used as the source of ultraviolet radiation in these studies. Carroll (ref. 5) has previously reported on the fact that the spectrum of the BH-6 lamp is not completely similar to the solar spectrum. Figure 2 shows the ratio of the lamp intensity (at distance of 25 cm) to solar intensity (at 1 A.U.) for different wavelengths in the 0.22- to 0.40-micron region. The cumulative average lamp intensity for this wavelength range is approximately 3 times the solar intensity. This figure is based on the geometry of this system and the manufacturer's data for BH-6 lamps (ref. 6). During use and aging BH-6 lamps often form an uneven milky film on the surface of the quartz capillary. The decay in the intensity with use is not equal for all wavelengths (ref. 5). The lamps were rotated about their axes to reduce intensity nonuniformities arising from inhomogeneities in the quartz envelope and the uneven film buildup. The relative intensities of the BH-6 lamps were monitored during each run with a Westinghouse SM-200 ultraviolet photometer. The individual lamps were selected and changed as necessary so as to maintain relative intensities within 15 percent of a nominal intensity of 3 times solar intensity.

EFFECT OF ULTRAVIOLET RADIATION

The results of the ultraviolet stability tests on the spectral absorptance α_λ are shown in figures 3 through 7. These measurements of α_λ were made within 4 hours after the samples were removed from the ultraviolet-vacuum chamber. The solar absorptances of the irradiated coatings were also determined periodically during the subsequent 3 months of exposure to air. The stable coatings, ZnO-Potassium Silicate and TiO_2-Silicone resin showed little significant change in α_s with air aging after the ultraviolet test. In the cases of the unstable coatings, Sb_2O_3-Potassium Silicate and TiO_2-Epoxy resin, a bleaching action was noted during air aging. This decrease in α_s (bleaching) after exposure to air was greater for the irradiated TiO_2-Epoxy than for the comparable Sb_2O_3-Potassium Silicate.

A comparison of figures 3 and 4 illustrates the U.V. effects on a stable pigment $\left(TiO_2\right)$ in stable silicone and unstable epoxy vehicles. The converse is shown by comparing figures 5 and 6 which illustrate the U.V. effect on a stable potassium silicate vehicle which contains unstable antimony oxide pigment in one case and stable zinc oxide pigment in the other. The effect of ultraviolet radiation on α_λ for Alodine 401 irradiated at different temperatures (ref. 7) is shown in figure 7. The increase in α_s for the test at 0° C was unexpected and is yet to be adequately explained. It may be due to photochemical reactions with some entrapped water which would be less volatile at the lower temperature. The ratio α_s/ϵ for the Alodine samples irradiated at 0° C was found to decrease with irradiation time as a result of an increase in thermal emittance ϵ which more than compensated for the increase in α_s. A comparison of the changes in the ratio of solar absorptance after exposure to ultraviolet radiation to the

initial solar absorptance α_s/α_{s_O} for the five coatings is shown in figure 8. The specific changes in α_s/α_{s_O} for each coating as well as the coating thickness and specimen temperature during individual tests are shown in figures 9 to 13. The individual coating thickness and specimen temperatures for each specimen are shown directly above the respective points on the plot of α_s/α_{s_O} versus ultraviolet exposure time. The accelerated exposures are not intended to represent useful lifetimes for satellites but do provide an indication of relative coating stability within reasonable limits of laboratory testing. Several deviations from a smooth curve relationship were noted in figures 9 through 13 and are attributed in large part to variation in coating thickness and specimen temperature during exposure. Coating thicknesses of the four paints were measured with a Dermitron, Model 2 Eddy Current Thickness Tester and checked with micrometer measurements after all U.V. testing and reflectance measurements were completed. Several of the test specimens showed differences in thickness which resulted in different initial values of α_s and may be partially responsible for somewhat erratic results after ultraviolet exposure. The variation in initial α_s as a function of thickness for the four paints is illustrated in figure 14. A few specimens showed considerable deviation from the smooth curves shown; generally, the ultraviolet stability of these specimens also deviated from that of their companion specimens.

EFFECT OF GAMMA RADIATION

The high-energy ionizing radiation stability of thermal control surfaces has been little studied compared to their ultraviolet stability although the coloring of glasses, plastic film, and alkali halides upon exposure to high-energy ionizing radiation are well-known phenomena. A brief series of tests was conducted to determine the extent of change in α_s produced by high-energy gamma radiation. Gamma radiation from a Cobalt-60 source offers a convenient means of simulating the effects rather than the environment (electrons and protons) of space. The materials used in these tests were coatings associated with OSO I and OSO II thermal control experiments and were supplied by Carr Neel (NASA Ames).

The coating specimens were placed in Pyrex tubes and outgassed for a minimum of 12 hours at 5×10^{-7} torr. After outgassing, the tubes were sealed under vacuum and irradiated with gamma rays from a Cobalt-60 source (Gamma-220 Cell) (ref. 8) at a dose rate of 1.6 Megarad/hour. The ambient temperature in the Gamma-220 Cell was 47° C. No attempt was made to cool the test specimens. Following irradiation, the Pyrex tubes were opened under argon. The reflectance of each irradiated coating was determined within 1 hour after opening of its Pyrex tube.

The results are summarized in Table II. In all cases the solar absorptance increased upon exposure to the 1.33 and 1.17 MEV gamma rays from the Cobalt-60 source. A direct comparison of the effects of gamma and ultraviolet radiations

on the solar absorptance is not practical at this time since the specimens used were not identical and the equivalent energies absorbed are not well-resolved. A relative comparison can be made based on the approximate equivalent exposure in space. A gamma dose of 77 Megarad $(7.7 \times 10^9 \text{ ergs/g(C)})$ approximates the surface dose at the end of 12 weeks in the inner Van Allen belt (ref. 9) and a dose of 385 Megarad approximates 57 weeks exposure. In a relative comparison of ultraviolet effects at 2 weeks equivalent sun exposure of U.V. with an exposure of 12 weeks equivalent inner belt absorbed dose of high-energy ionizing (gamma) radiation, the Titanium Dioxide-Epoxy and the Antimony Oxide-Potassium Silicate coatings were found to be more susceptible to damage from ultraviolet radiation than from gamma radiation.

As a first approximation the same does not hold true for the TiO_2-Silicone coating which underwent a change in α_s equal to or greater than that obtained by extrapolation of the change in α_s due to ultraviolet radiation. While the gamma radiation has a higher energy and is more penetrating than the ultraviolet radiation, it is not selectively absorbed as is the U.V. The selective absorption of the ultraviolet makes this source of radiation much more effective in causing change in α_s.

EFFECT OF GAMMA RADIATION ON THERMAL CONTROL COATINGS

TABLE II

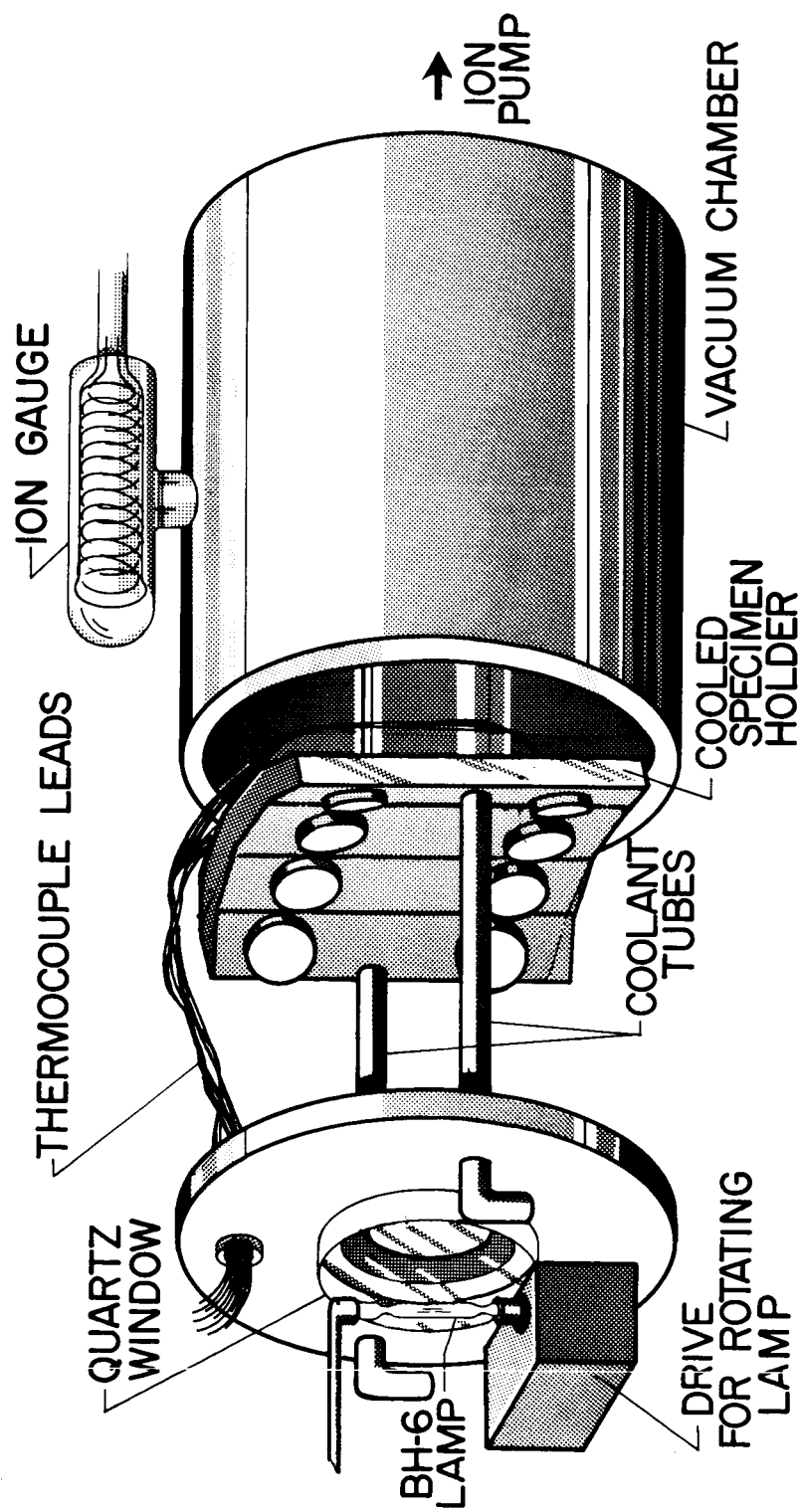| Coating		Solar absorptance, α_s			
		Dose, MRAD			
Pigment	Vehicle	0	77	0	385
Zinc oxide	Silicone plus catalyst	0.17	0.21	0.17	0.21
Zinc oxide	Silicone resin	.19	.22	.20	.23
Zinc oxide	Potassium silicate	.14	.18	.14	.18
Zinc sulfide	Silicone resin	.20	.23	.20	.23
TiO_2	Silicone film	.12	.24	.13	.23
TiO_2	Silicone resin	.25	.37	.25	.43
TiO_2	Epoxy resin	.20	.42	.20	.47
Zircon	Potassium silicate	.09	.15	.09	.15
Zirconium silicate	Potassium silicate	.06	.13	.07	.15
Lithium aluminum silicate	Sodium silicate	.09	.35	.10	.36
Antimony oxide	Potassium silicate	.26	.36	.25	.52

CONCLUSIONS

The environmental testing of thermal control coatings is complicated by such variables as coating thickness and sample temperature during testing, both of which may significantly influence the degree of change in α_s during exposure to ultraviolet radiation. The influence of sample temperature is particularly significant in accelerated testing where the higher intensities can produce increased temperatures unless specifically compensated for by effective cooling.

Gamma radiation, used to simulate the effects of electrons and protons, generally changes α_s less than ultraviolet radiation when a comparison is made on the basis of equivalent time exposures in space. More attention should be given to additional studies of the effects of high-energy ionizing radiation on thermal-control coatings. These effects should be taken into account in the analysis of the results from thermal-control experiments aboard spacecraft, as well as in spacecraft design for long-term missions.
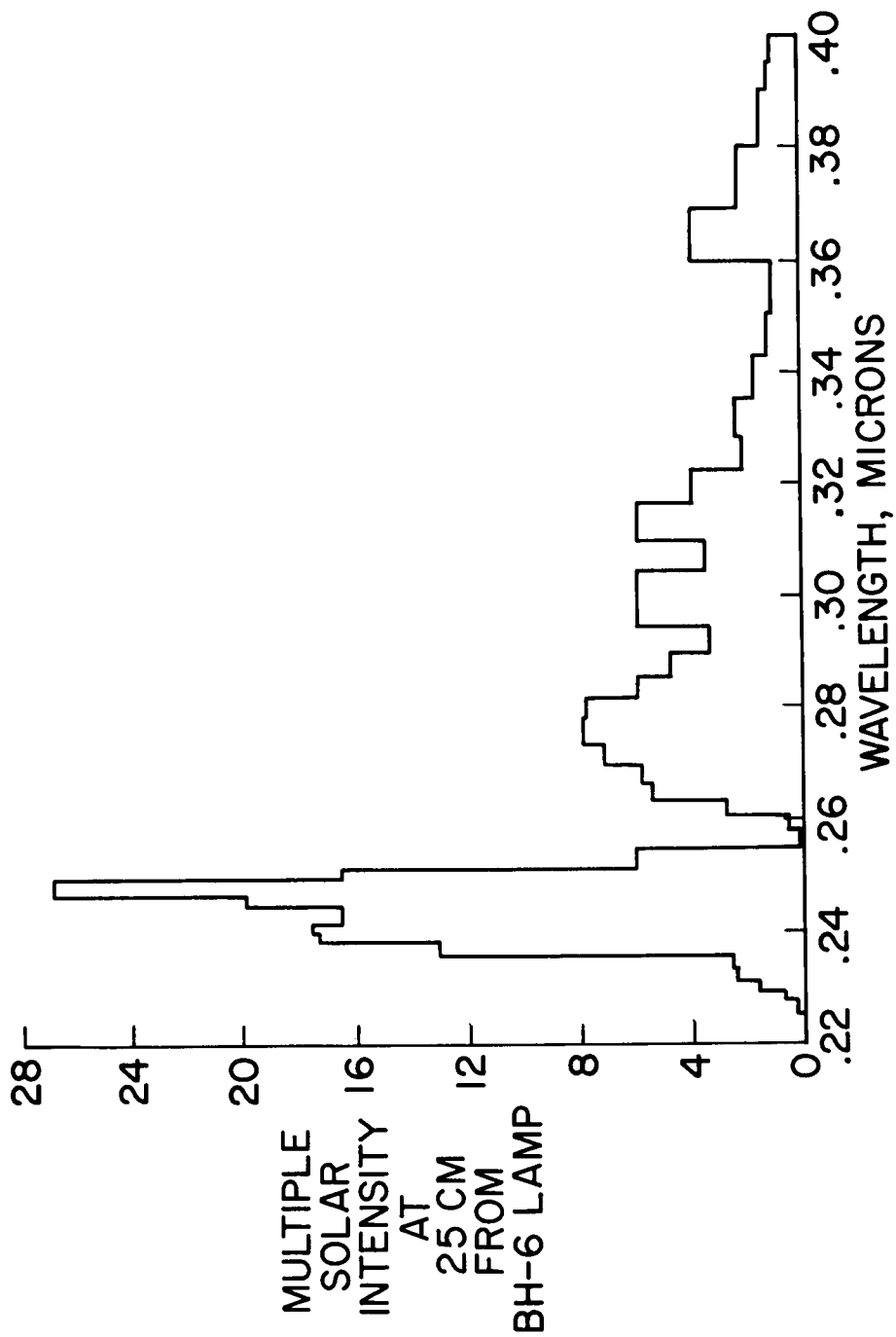
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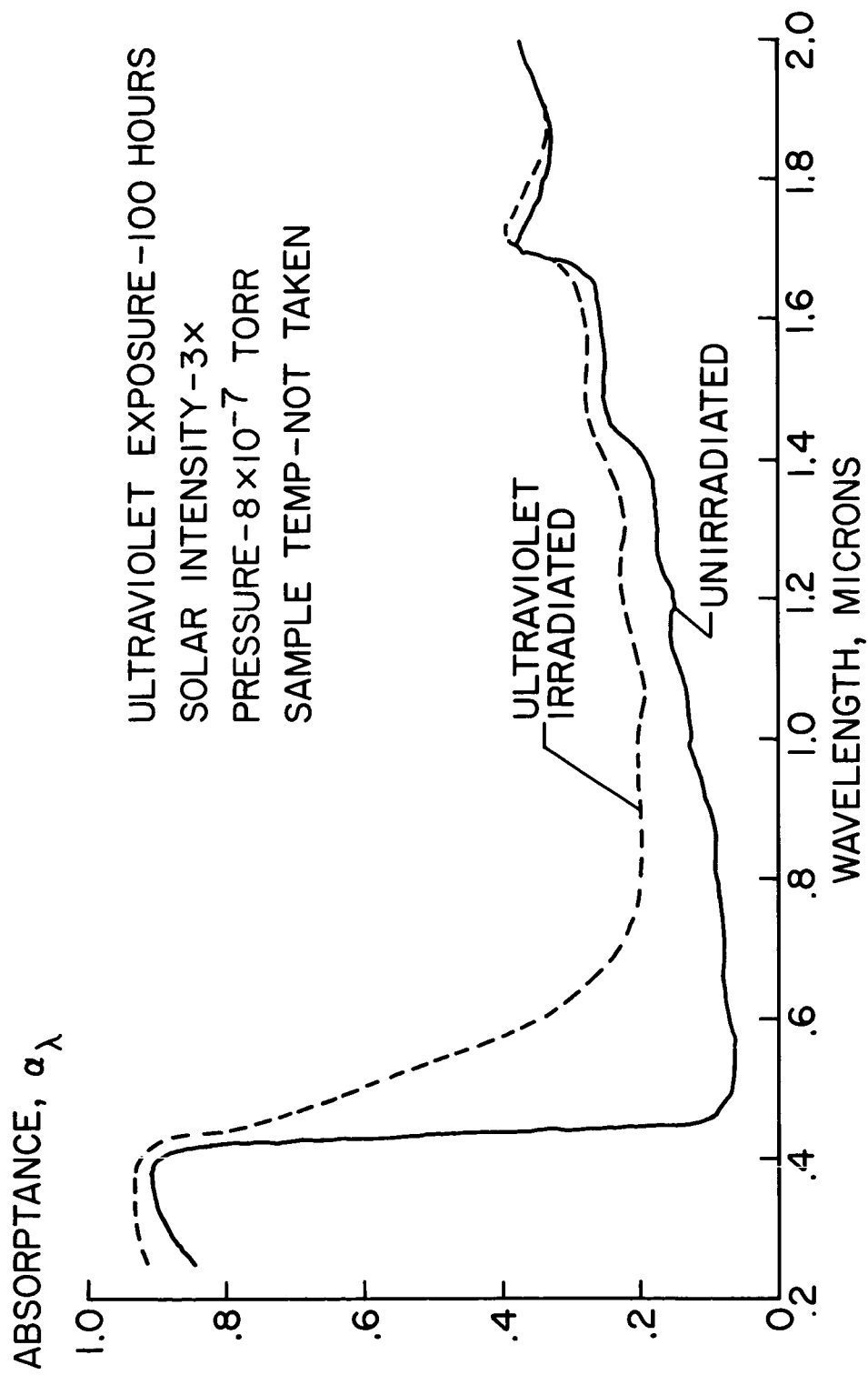
ION GAUGE

ION PUMP

VACUUM CHAMBER

THERMOCOUPLE LEADS

COOLED SPECIMEN HOLDER

COOLANT TUBES

QUARTZ WINDOW

BH-6 LAMP

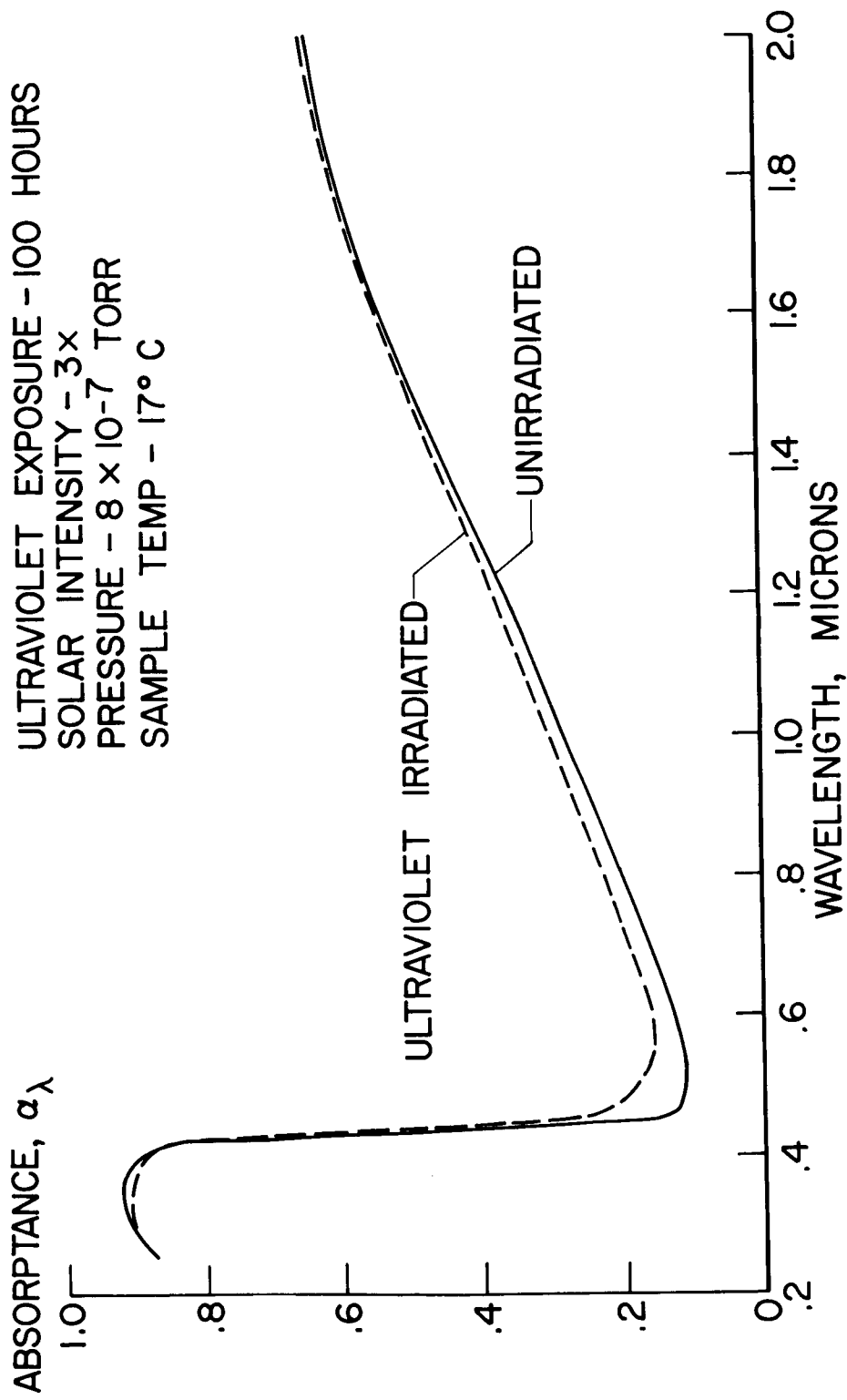DRIVE FOR ROTATING LAMP

NASA

Figure 1.- Ultraviolet-vacuum chamber.

Figure 2. - Multiple solar intensities at selected wavelengths for BH-6 mercury arc.

NASA

Figure 3.- Influence of ultraviolet on spectral absorptance of titanium dioxide-epoxy.
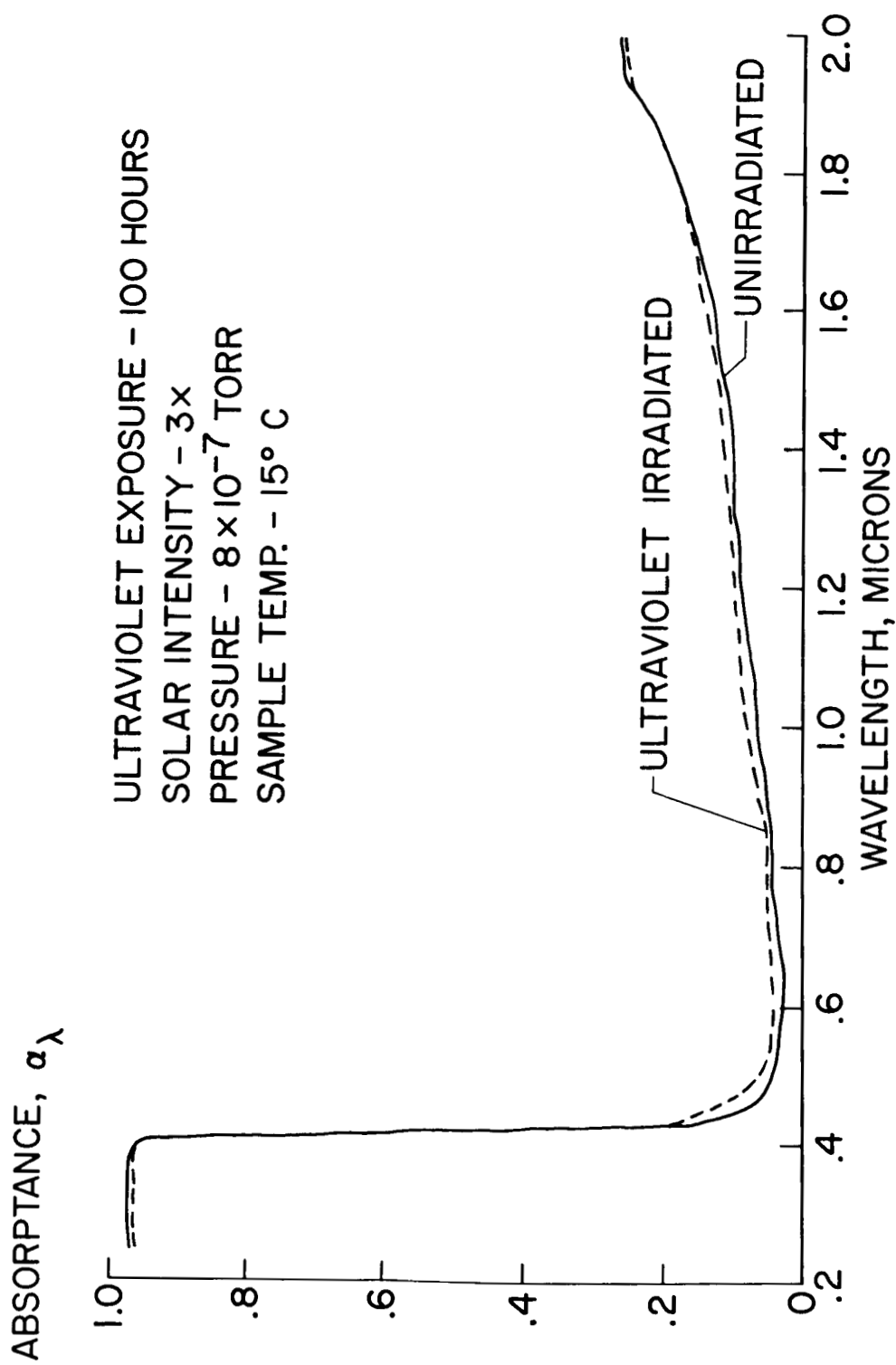
ABSORPTANCE, α_λ

ULTRAVIOLET EXPOSURE-100 HOURS
SOLAR INTENSITY-3×
PRESSURE-8×10⁻⁷ TORR
SAMPLE TEMP-NOT TAKEN

ULTRAVIOLET
IRRADIATED

UNIRRADIATED

WAVELENGTH, MICRONS

NASA

ULTRAVIOLET EXPOSURE – IOO HOURS
SOLAR INTENSITY – 3×
PRESSURE – 8×10^{-7} TORR
SAMPLE TEMP – 17° C

ABSORPTANCE, α_λ

1.0

.8

.6

.4

.2

0
.2 .4 .6 .8 I.O I.2 I.4 I.6 I.8 2.0

WAVELENGTH, MICRONS

ULTRAVIOLET IRRADIATED

UNIRRADIATED

NASA

Figure 4. – Influence of ultraviolet on spectral absorptance of titanium dioxide-silicone.
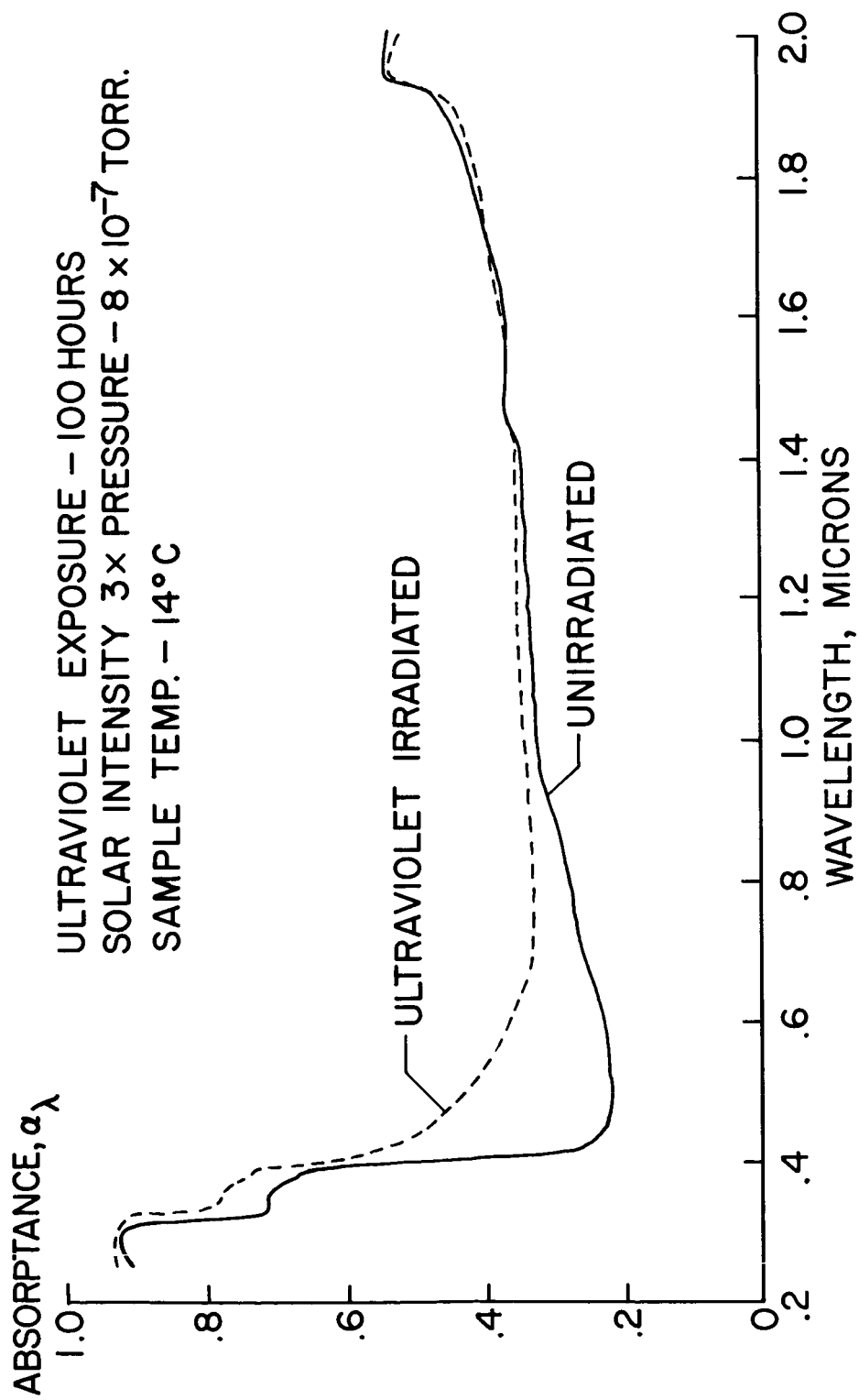
Figure 5.- Influence of ultraviolet on spectral absorptance of antimony oxide-potassium silicate.

ABSORPTANCE, α_λ

ULTRAVIOLET EXPOSURE – 100 HOURS
SOLAR INTENSITY – 3×
PRESSURE – 8×10^{-7} TORR
SAMPLE TEMP. – 15° C

ULTRAVIOLET IRRADIATED

UNIRRADIATED

WAVELENGTH, MICRONS

NASA

Figure 6.- Influence of ultraviolet on spectral absorptance of zinc oxide-potassium silicate.
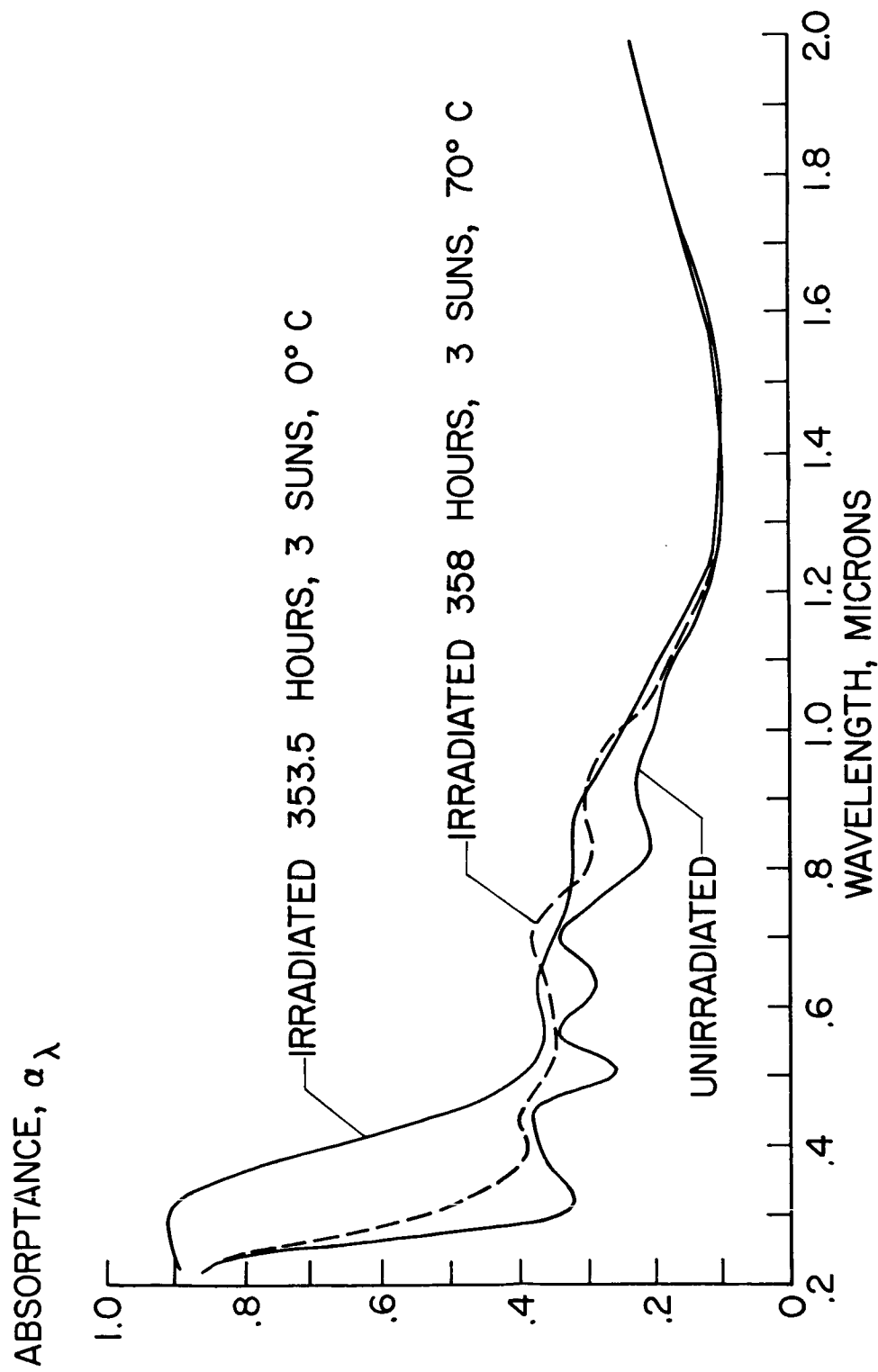
Figure 7.- Influence of ultraviolet on spectral absorptance of Alodine 401.
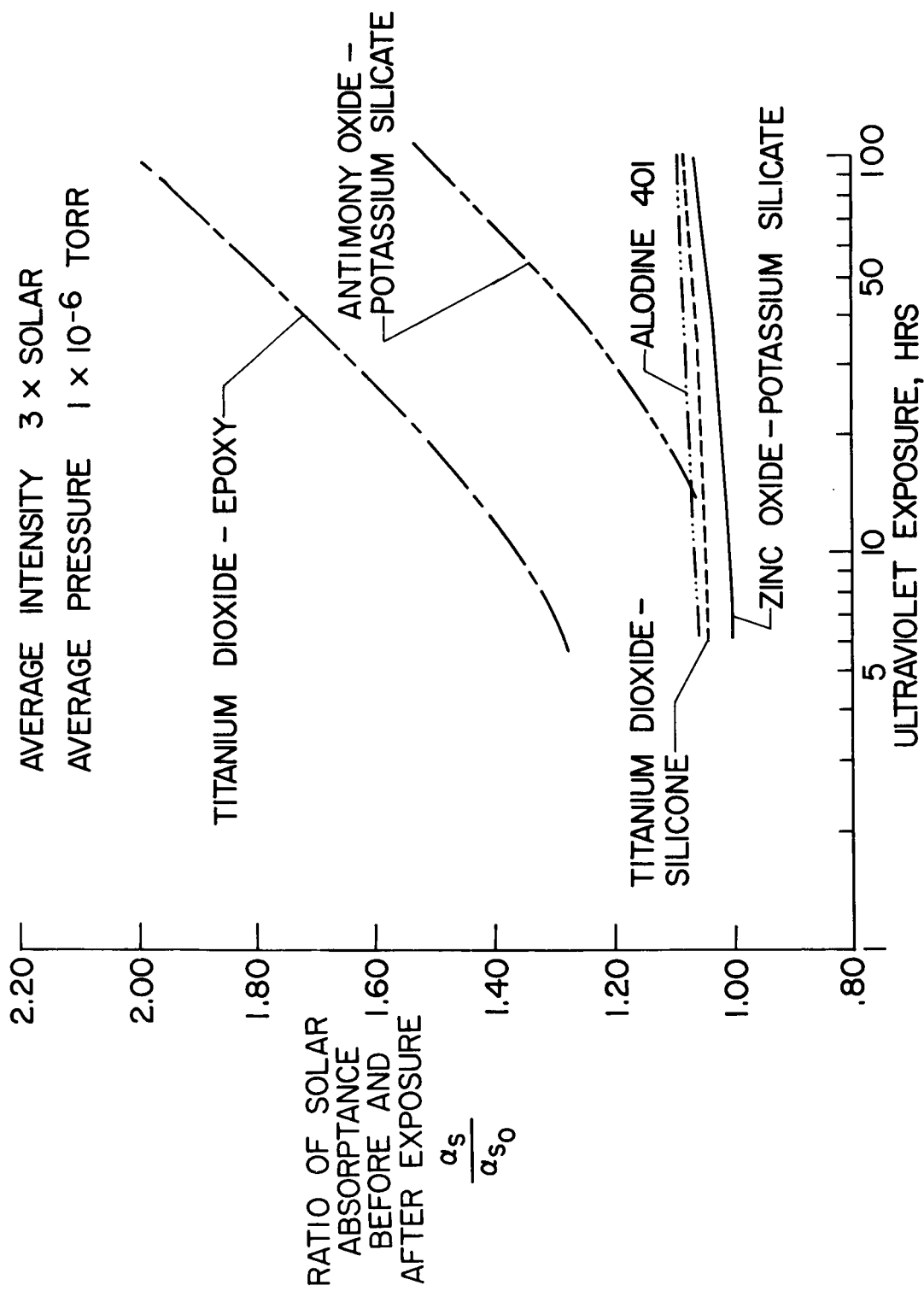
Figure 8.- Comparative effect of ultraviolet and vacuum exposure on five selected coatings.
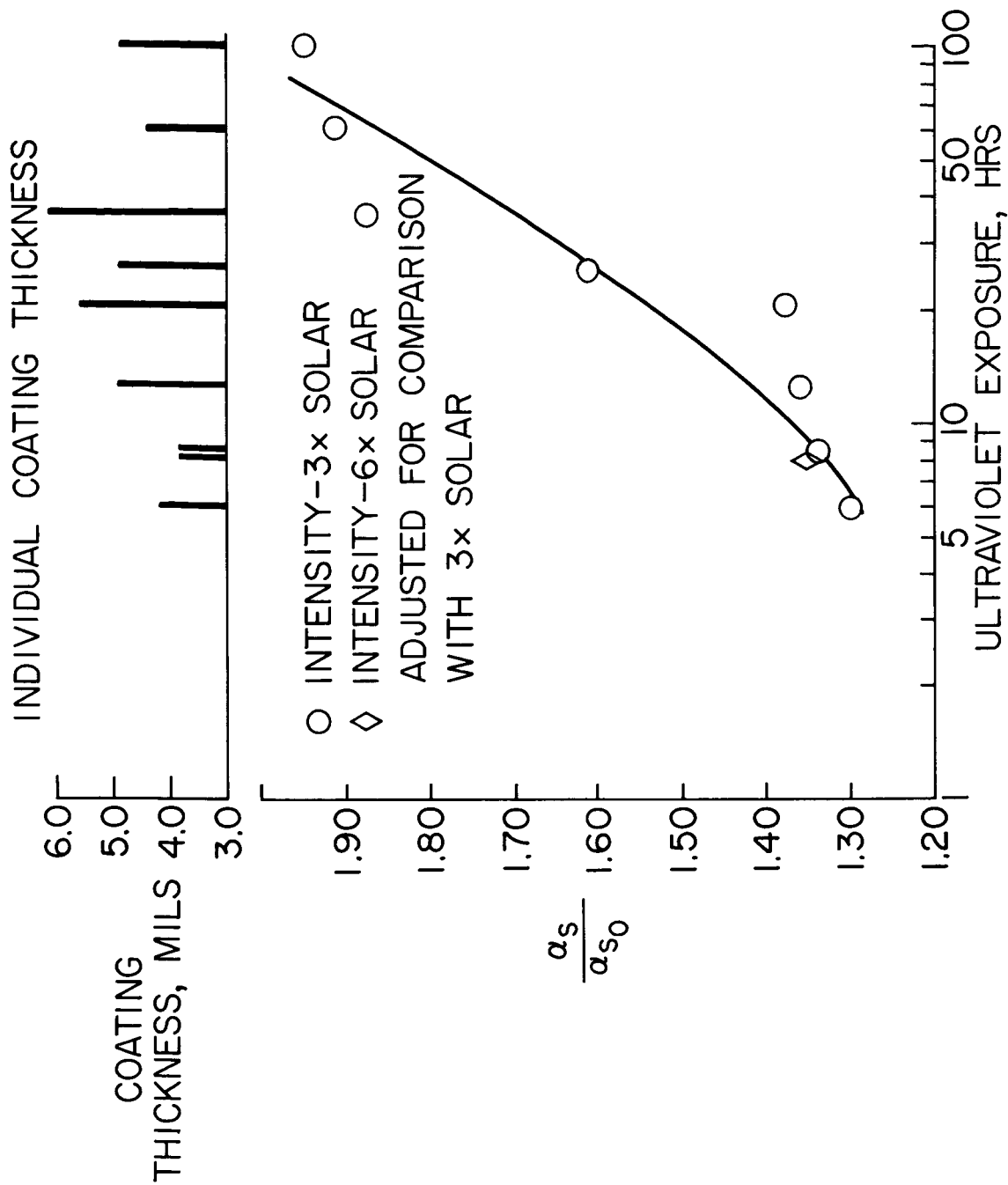
Figure 9.- Effect of ultraviolet irradiation on titanium dioxide-epoxy.
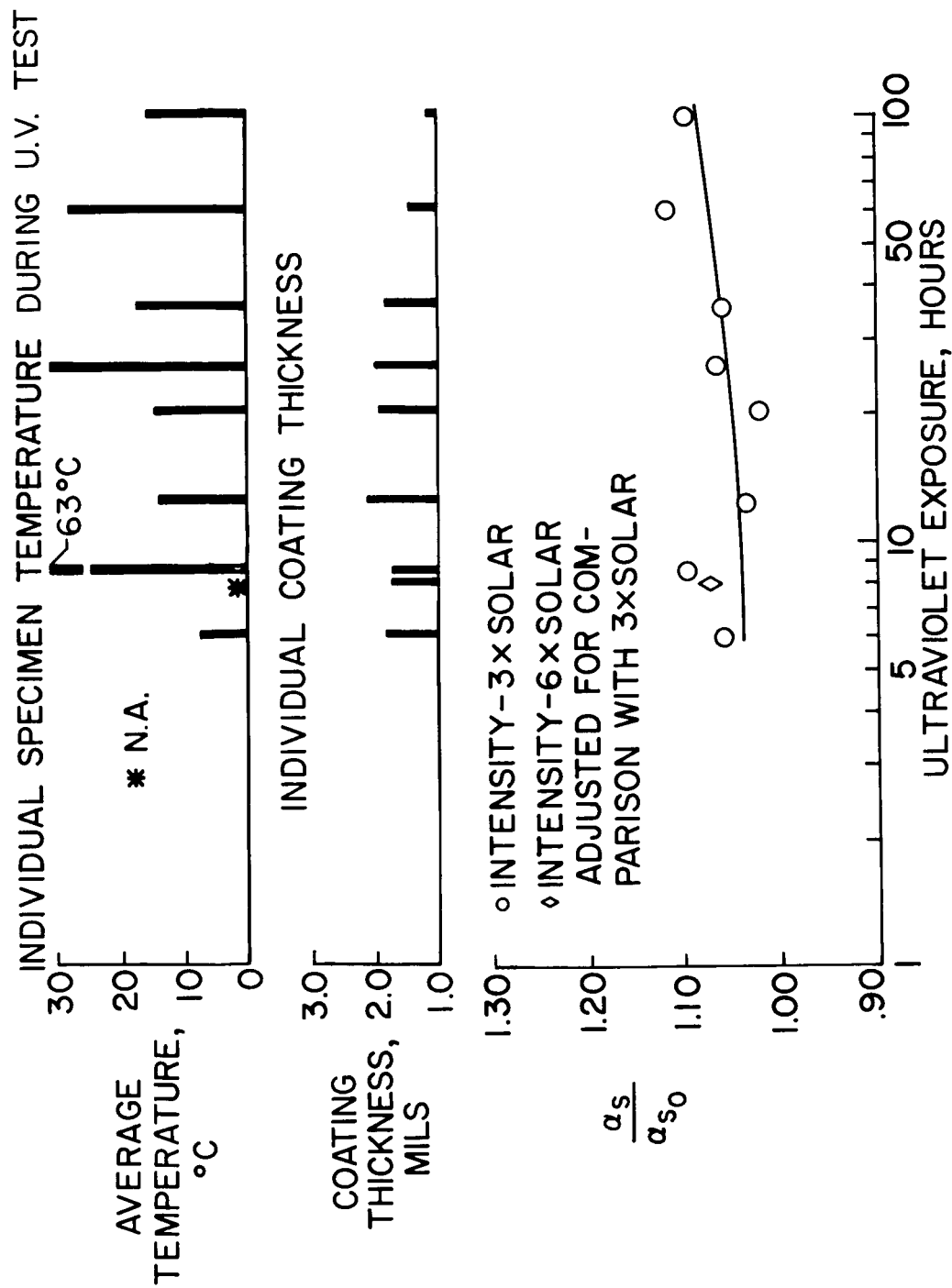
Figure 10. - Effect of ultraviolet irradiation on titanium dioxide-silicone.

NASA

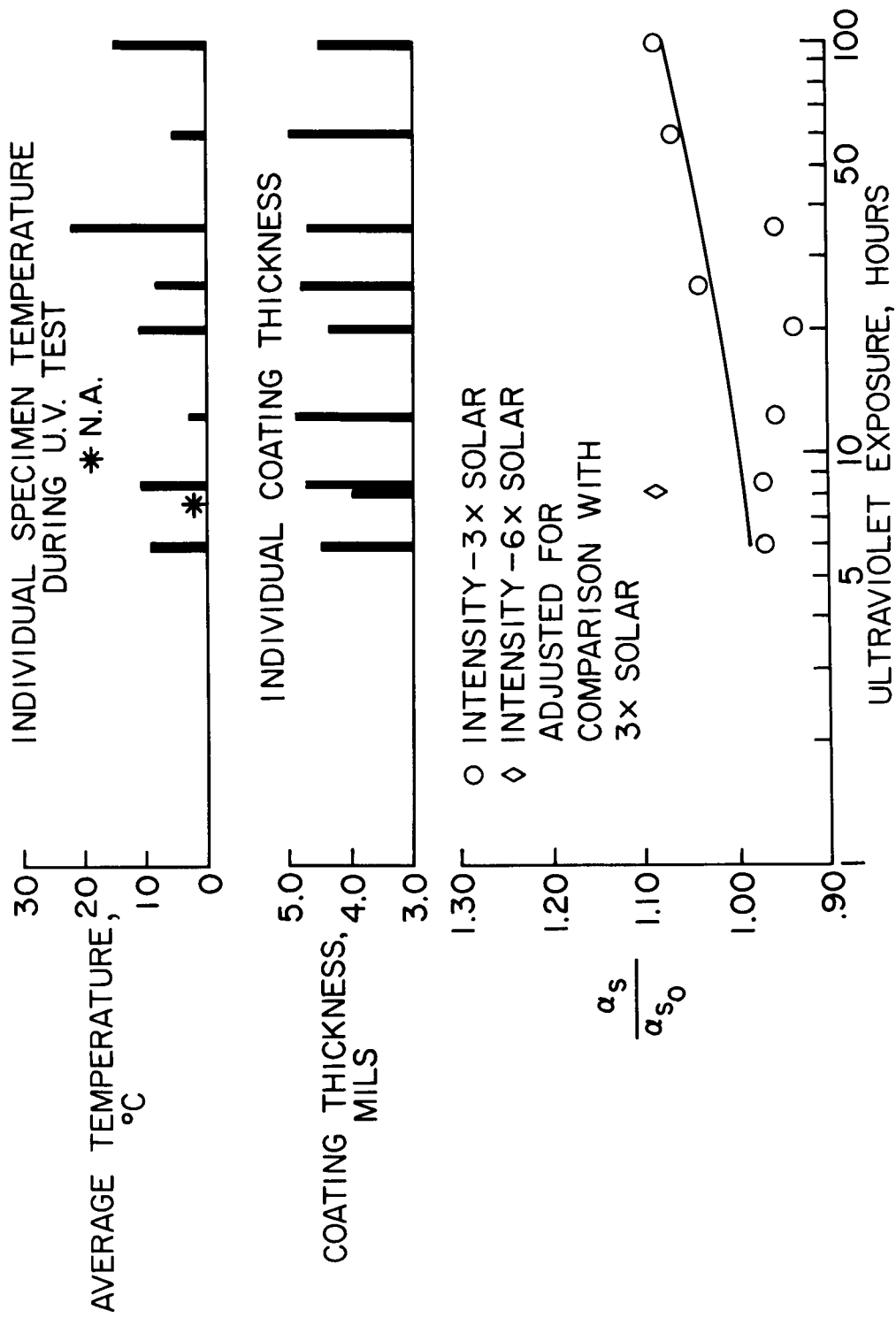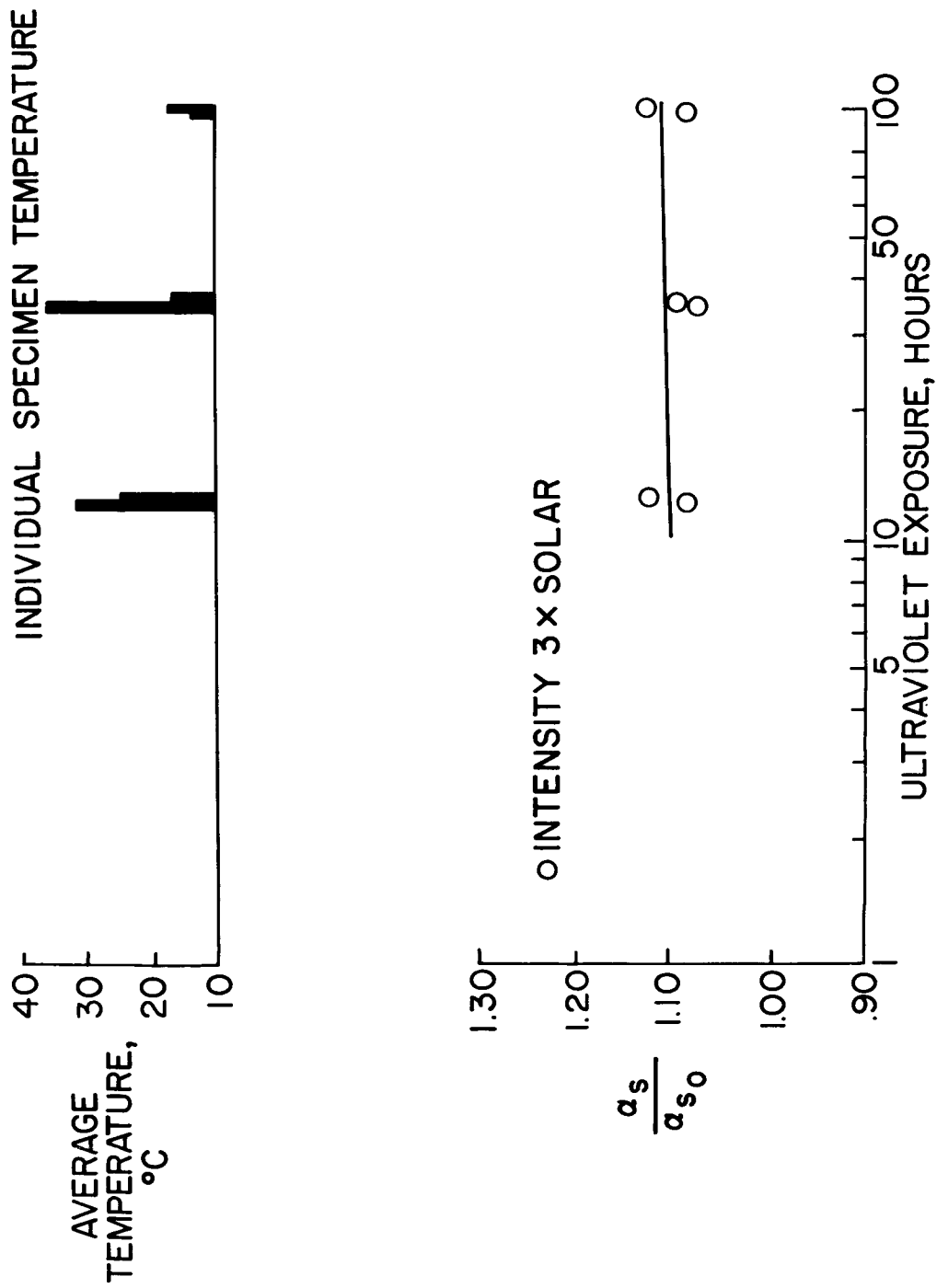Figure 11.- Effect of ultraviolet irradiation on antimony oxide-potassium silicate.

NASA

Figure 12.- Effect of ultraviolet irradiation on zinc oxide–potassium silicate.

NASA

INDIVIDUAL SPECIMEN TEMPERATURE

AVERAGE
TEMPERATURE,
°C

40

30

20

10

○ INTENSITY 3 × SOLAR

$\dfrac{\alpha_s}{\alpha_{s_0}}$

1.30

1.20

1.10

1.00

.90

5

10

50

100

ULTRAVIOLET EXPOSURE, HOURS

NASA

Figure 13.- Effect of ultraviolet irradiation on Alodine 401 (A-12 laminate).
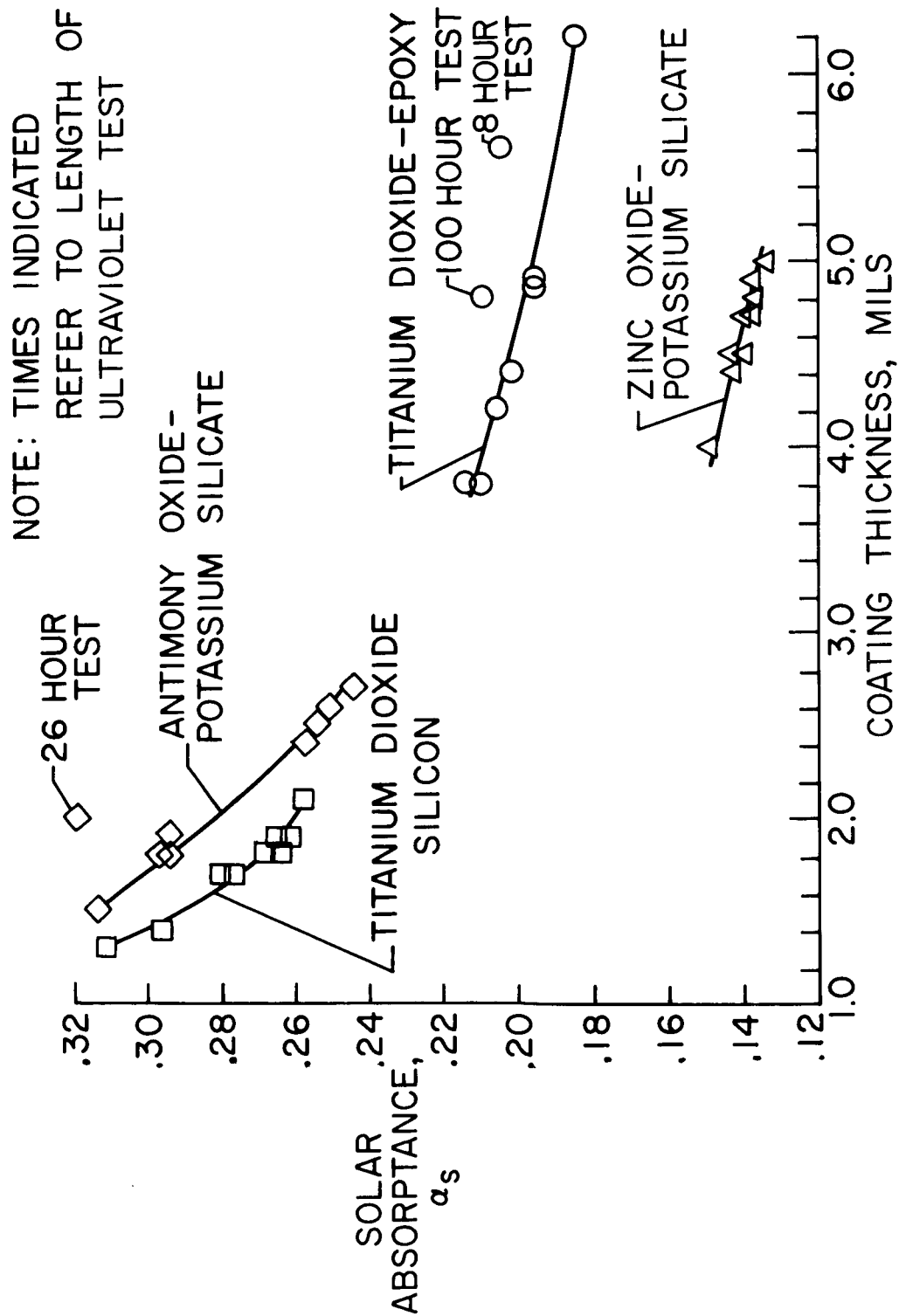
Figure 14.- Effect of thickness on solar absorptance.